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**Notes:**

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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**FULL CONTENTS**

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**[Claim(s)]**

[Claim 1] HC sorbent which comes on a carrier from the powdered inorganic crystal nature molecular sieve which adsorbs hydrocarbon in exhaust gas is supported. The 1st catalyst bed which uses Pd as catalyst metal is formed in each surface of the above-mentioned HC adsorbent particle. The catalyst for exhaust gas depuration of the internal combustion engine characterized by forming the rare-earths oxide layer which uses a rare-earths oxide as the main ingredients on the 1st catalyst bed of the above, and forming the 2nd catalyst bed which uses either [ at least ] Pt or the Rh(s) as catalyst metal on the above-mentioned rare-earths oxide layer.

[Claim 2] In the catalyst for exhaust gas depuration of the internal combustion engine indicated to Claim 1, the above-mentioned rare-earths oxide is CeO<sub>2</sub>. Catalyst for exhaust gas depuration of the internal combustion engine which comes out and is characterized by a certain thing.

[Claim 3] In the catalyst for exhaust gas depuration of the internal combustion engine indicated to Claim 3, the above-mentioned carrier is a MONORISU carrier, and it is the above-mentioned CeO<sub>2</sub> per these 1l. of carriers. Catalyst for exhaust gas depuration of the internal combustion engine characterized by quantity being 15-100g.

[Claim 4] The catalyst for exhaust gas depuration of the internal combustion engine characterized by the above-mentioned HC sorbent being crystalline aluminosilicate in the catalyst for exhaust gas depuration of the internal combustion engine indicated to Claim 1.

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**[Detailed Description of the Invention]**

[0001]

[Industrial Application] This invention relates to the catalyst for exhaust gas depuration of an

internal combustion engine.

[0002]

[Description of the Prior Art] As a catalyst which purifies HC (hydrocarbon), CO (carbon monoxide), and NO<sub>x</sub> (nitrogen oxides) in the exhaust gas of an internal combustion engine What prepares the 1st catalyst bed which uses a zeolite as the main ingredients on a MONORISU carrier, and prepares the 2nd catalyst bed which uses as the main ingredients \*\*\*\*\* equipped with oxidation reduction ability on this 1st catalyst bed is known (refer to JP,H2-56247,A). To the 1st catalyst bed of the above, if needed The precious metals, such as Pt, Pd, and Rh, and CeO<sub>2</sub> (ceria), The rare-earths oxide of La<sub>2</sub> O<sub>3</sub> (Lantana) etc. is supported, the precious metals, such as Pt, Pd, and Rh, are supported by the alumina coat layer, and, as for the 2nd catalyst bed of the above, the above-mentioned rare-earths oxide, a zirconium dioxide, etc. are supported if needed.

[0003] The above-mentioned catalyst for exhaust gas depuration in the time between [ of an internal combustion engine ] the colds when [ and ] HC in exhaust gas is adsorbed by the zeolite of the 1st catalyst bed of the above when it is in the status that an air-fuel ratio is rich, and exhaust gas temperature and the degree of catalyst temperature rise by warming up The 2nd catalyst bed of the above performs oxidization of HC and CO in HC desorbed from the 1st catalyst bed of the above, and exhaust gas, and reduction of NO<sub>x</sub>.

[0004]

[Problem to be solved by the invention] Although Pt and Pd have [ this invention person ] high oxidization ability about the function as a catalyst metal of Above Pt, Pd, and Rh, compared with it, oxidization ability of Rh is low, Therefore, the knowledge that decomposition of NO<sub>x</sub> progressed comparatively efficiently with oxidization of HC when Pt's and Pd's being effective in depuration of HC, and Pt and Rh are combined had been acquired.

[0005] However, in the above-mentioned conventional technology, when three persons of Above Pt, Pd, and Rh are used together as the catalyst metal of the 1st catalyst bed of the above, or a catalyst metal of the 2nd catalyst bed, there is a problem that both HC purifying rate and a NO<sub>x</sub> purifying rate fall compared with the case where Pt and Rh are used together. This is considered for interfering each other so that Pt, Rh, and Pd may check a mutual catalyst function. On the other hand, although it is possible to separate Pd from Pt or Rh by supporting Pd to the 1st catalyst bed and for example making the 2nd catalyst bed support Pt and Rh, respectively, Pd, Pt, and Rh contact in the interface of the 1st catalyst bed and the 2nd catalyst bed, and a good result is not necessarily obtained.

[0006] Then, it tends to raise a NO<sub>x</sub> purifying rate while this invention combines Above Pd with Above Pt or Rh so that the original catalyst function may be exhibited, and it raises HC purifying rate after the time between [ of an internal combustion engine ] the colds, and warming up.

[0007]

[Means for Solving the Problem and its Function] When this invention person makes the layer of a rare-earths oxide intervene between the 1st catalyst bed which uses Pd as catalyst metal, and the 2nd catalyst bed which uses Pt or Rh as catalyst metal as a result of adding various experiments and examination to the above-mentioned technical problem Each of such catalyst metal and HC sorbent can exhibit effectively the function of the original which it has, and the desired end can be attained, When the 1st catalyst bed of the above, a rare-earths oxide layer, and the 2nd catalyst bed are especially formed in each surface of HC adsorbent particle, it finds out that a good result is obtained, and it comes to complete this invention. Invention concerning each claim is explained concretely hereafter.

[0008] <invention concerning Claim 1> -- [ this invention / HC sorbent which comes on a carrier from the powdered inorganic crystal nature molecular sieve which adsorbs hydrocarbon in exhaust gas is supported, and ] The 1st catalyst bed which uses Pd as catalyst metal is formed in each surface of the above-mentioned HC adsorbent particle. It is the catalyst for exhaust gas depuration of the internal combustion engine characterized by forming the rare-earths oxide layer which uses a rare-earths oxide as the main ingredients on the 1st catalyst bed of the above, and forming the 2nd catalyst bed which uses either [ at least ] Pt or the Rh(s) as catalyst metal on the above-mentioned rare-earths oxide layer.

[0009] In the invention concerned, at the time between [ of an internal combustion engine ] the colds, HC sorbent is adsorbed in HC in exhaust gas, and the discharge which is not purified HC is prevented. [ if exhaust gas temperature and the degree of catalyst temperature rise by warming up, desorption of HC by which each HC sorbent was adsorbed will start, but ] Since the 1st catalyst bed which uses Pd as catalyst metal is formed in the surface of each of this HC adsorbent particle, the desorption HC concerned contacts Pd easily and, for this reason, exhibits efficiently the catalyst function in which Pd carries out oxidative degradation of the HC concerned. Moreover, also in the 2nd catalyst bed, although the \*\*\*\*ing above-mentioned HC is decomposed by Pt or Rh, this Pt and Rh are a catalyst metal effective in depuration of NO<sub>x</sub> in exhaust gas, and exhibit the catalyst function as for which a returned part understands NO<sub>x</sub> by using as a reducing agent HC decomposed [ which decomposes and above-\*\*\*\*s ].

Moreover, oxidative degradation also of HC and CO which are newly discharged from an internal combustion engine is carried out with the catalyst metal of the 1st catalyst bed and the 2nd catalyst bed, and the reductive cleavage of NO<sub>x</sub> advances with such oxidation reaction.

[0010] On the other hand, the function of the barrier which prevents Pd from Above Pt, or Rh and Pd each other in the rare-earths oxide which intervenes between the 1st catalyst bed of the above and the 2nd catalyst bed is achieved, and the fall of the catalyst function by the interaction between such catalyst metal is prevented. [ on the other hand, if such barrier also bars diffusion of HC in exhaust gas, the 1st catalyst bed will be used effective in adsorption

and decomposition of HC but ] The barrier of the invention concerned is a rare-earths oxide, though this rare-earths oxide bars diffusion of HC a little, it is [ that extent ] low, and it does not become the trouble of adsorption of HC in the exhaust gas by HC sorbent of the 1st catalyst bed. This rare-earths oxide is O<sub>2</sub> on the contrary. Since it has the storage effect, it will contribute effective in oxidization of HC in the 1st catalyst bed and the 2nd catalyst bed.

[0011] A deer is carried out, in the invention concerned, since the 1st catalyst bed of the above, a rare-earths oxide layer, and the 2nd catalyst bed are formed in each surface of HC adsorbent particle, the oxidative degradation of HC and reduction decomposition of NO<sub>x</sub> are produced on each HC adsorbent particle, and each purifying rate becomes high.

[0012] As the above-mentioned carrier, it may be a MONORISU carrier here, or you may be the carrier of a pellet type. moreover, as an inorganic crystal nature molecular sieve as the above-mentioned HC sorbent the aluminosilicate (Y zeolite --) using aluminum as a metal which forms the frame (crystal lattice) of a crystal Various kinds of zeolites, such as mordenite, ZSM5, and a beta zeolite, It can replace with aluminum or various things, such as other metal content silicate of crystalline material porosity using other metal, such as Ga, Ce, Mn, and Tb, a thing which further almost consists only of silica, and a thing which does not contain Si, can be adopted with aluminum.

[0013] <invention concerning Claim 2> -- in the catalyst for exhaust gas depuration of the internal combustion engine with which this invention is indicated to above-mentioned Claim 1 -- the above-mentioned rare-earths oxide -- CeO<sub>2</sub> it is -- it is the catalyst for exhaust gas depuration of the internal combustion engine characterized by things.

[0014] In this invention, it is CeO<sub>2</sub> as a rare-earths oxide. Using is this CeO<sub>2</sub>. O<sub>2</sub> The storage effect is high and it is because it becomes advantageous to the oxidative degradation of HC.

[0015] <invention concerning Claim 3> -- in the catalyst for exhaust gas depuration of the internal combustion engine with which this invention is indicated to above-mentioned Claim 3, the above-mentioned carrier is a MONORISU carrier -- the above-mentioned CeO<sub>2</sub> per these 1l. of carriers It is the catalyst for exhaust gas depuration of the internal combustion engine characterized by quantity being 15-100g.

[0016] In the invention concerned, it is because it becomes advantageous to contact with exhaust gas and a catalyst bed to use a MONORISU carrier, and is because the small size and the weight saving of a catalyst can be attained and there is also little elevation of back pressure. Moreover, CeO<sub>2</sub> per 1l. of carriers It is for making quantity or more into 15 securing the effect which intercepts Pd of the 1st catalyst bed, Pt of the 2nd catalyst bed, or Rh. CeO<sub>2</sub> Quantity shall be 100g or less because it will become disadvantageous for diffusion of HC from the 2nd catalyst bed to the 1st catalyst bed if the quantity increases more than this.

[0017] <invention concerning Claim 4> -- this invention is the catalyst for exhaust gas depuration of the internal combustion engine characterized by the above-mentioned HC

sorbent being crystalline aluminosilicate in the catalyst for exhaust gas depuration of the internal combustion engine indicated to above-mentioned Claim 1.

[0018] In the invention concerned, as an HC sorbent, this has a heat-resisting property and the above-mentioned aluminosilicate is used because the HC adsorption capacity is high.

[0019]

[Effect of the Invention] The 1st catalyst bed which uses Pd as catalyst metal on each HC adsorbent particle according to invention concerning Claim 1, [ permitting diffusion of HC from the 2nd catalyst bed to the 1st catalyst bed, since the 2nd catalyst bed which uses Pt or Rh as catalyst metal, and a rare-earths oxide layer were formed and the rare-earths oxide layer was made to intervene between the 1st catalyst bed and the 2nd catalyst bed ] [ being able to avoid that Pt, or Rh and Pd interfere each other, fully being able to demonstrate the catalyst function of Pd, and preventing the discharge which is not purified at the time between the colds HC ] this -- since HC and NO<sub>x</sub> can be purified efficiently and decomposition depuration of HC and NO<sub>x</sub> is moreover performed on each HC adsorbent particle, high HC purifying rate and a high NO<sub>x</sub> purifying rate are acquired.

[0020] According to invention concerning Claim 2, it is CeO<sub>2</sub> as the above-mentioned rare-earths oxide. Since it used, it is this CeO<sub>2</sub>. O<sub>2</sub> [ high ] The storage effect can be used for the oxidative degradation of HC, and it becomes advantageous to improvement in HC purifying rate and a NO<sub>x</sub> purifying rate.

[0021] According to invention concerning Claim 3, it is the above-mentioned CeO<sub>2</sub>. Diffusing HC from the 2nd catalyst bed to the 1st catalyst bed, since quantity was considered as per [ 15-100g ] 1l. of MONORISU carriers, when avoiding contact with Pd of the 1st catalyst bed, Pt of the 2nd catalyst bed, or Rh, it becomes advantageous.

[0022] According to invention concerning Claim 4, since crystalline aluminosilicate was used as the above-mentioned HC sorbent, HC adsorption capacity of a catalyst increases and it becomes advantageous to improvement in HC purifying rate and a NO<sub>x</sub> purifying rate.

[0023]

[Working example] The work example of this invention is hereafter explained based on Drawings.

[0024] The wash coat of the proton type Y zeolite (cay van ratio 80) powder was carried out to the MONORISU carrier (400 cels /inch<sup>2</sup>) of the shape of a honeycomb made from cordierite as a preparation-HC sorbent of a <work-example 1>-catalyst. This wash coat sets the above-mentioned Y zeolite and hydrated alumina as a binder by the bulk density of 100:20, and produces a slurry by adding optimum dose of purified water and carrying out churning mixture. After making the above-mentioned carrier support Y zeolite of the specified quantity by repeating the process of immersing and pulling up the above-mentioned carrier to this slurry, blowing away an excessive slurry and drying, calcination of 500 degree-Cx 2 hours is

performed.

[0025] Next, the 1st catalyst bed was formed by making the above-mentioned wash coat layer support Pd by the sinking-in method. This sinking-in support infiltrates the palladium nitrate solution of prescribed concentration into the above-mentioned wash coat layer, and performs dryness and calcination (500 degree-Cx 2 hours).

[0026] Next, it is CeO<sub>2</sub> as a rare-earths oxide layer on the 1st catalyst bed of the above by dissolving a cerium nitrate in purified water, preparing cerium nitrate solution, infiltrating this cerium nitrate solution into the above-mentioned wash coat layer, and performing dryness and calcination. The layer was formed.

[0027] Next, the 2nd catalyst bed which uses Pt and Rh as catalyst metal was formed on [ two-layer ] Above CeO by mixing nitric acid platinum-P salt solution (dinitro diamine platinum (II) nitric acid aqueous acids) and nitric acid rhodium solution, and infiltrating this mixed solution into the above-mentioned wash coat layer.

[0028] Therefore, the catalyst structures of this example are the 1st catalyst bed 2 and CeO<sub>2</sub> to the surface of each HC adsorbent particle 1 on a carrier, as shown in drawing 1 . A layer 3 and the 2nd catalyst bed 4 had carried out lamination formation from the bottom at order.

[0029] With the method of preparation of the evaluation-[NO<sub>x</sub> depuration performance] above-mentioned catalyst of a catalyst, the amount of HC sorbent support of the 1st catalyst bed per 1l. of carriers - 130g, It is the amount of Pd support 7g and CeO<sub>2</sub> The amount of support was 36g and some kinds of catalysts which shall be mutually different in the amount of support which doubled Pt and Rh of the 2nd catalyst bed were prepared. Each rate of a bulk density of Pt and Rh was set to 5:1. And after heat-treating for these catalysts, each catalyst was included in mimesis exhaust gas circulation equipment, and the NO<sub>x</sub> purifying rate (NO<sub>x</sub> C400) in case the inlet gas temperature of each catalyst is 400 degrees C was investigated. The measurement conditions are as follows.

[0030] Heat-treatment; 900 degree-Cx 50 hours (inside of the atmosphere)

Mimesis exhaust gas; ingredient It is N<sub>2</sub>, CO<sub>2</sub>, CO, C<sub>3</sub> H<sub>6</sub>, O<sub>2</sub>, H<sub>2</sub>, NO, however A/F=15.0, and H<sub>2</sub> O is added 10%.

space velocity; -- heating-rate [ of SV=60000h<sup>-1</sup> mimesis exhaust gas ]; -- a part (\*\*\*\* from room temperature to 500 degrees C) for 30-degree/

[0031] A/F value of mimesis exhaust gas were set to the lean side rather than theoretical air fuel ratio, in order that a performance difference might tend to have come out of the depuration of NO<sub>x</sub> by a catalyst to each catalyst as a difficult thing.

[0032] A result is combined with the thing of a comparative example 1, and is shown in drawing 2 . After a comparative example 1 performs the wash coat of HC sorbent to the same carrier as a work example, it performs sinking-in support in order of CeO<sub>2</sub> ->Pd->Pt and Rh, and differs in the order of sinking in, but it is the same as a work example. [ of the wash coat

method, the sinking-in method, and material ] Moreover, as for the amount of HC sorbent support of a comparative example 1, 130g/L and the amount of Pd support are 7g/L and CeO<sub>2</sub>. The amount of support which doubled 36g/L, and Pt and Rh for the amount of support is 1.6g/L.

[0033] According to this figure, in the work example, it turns out that a high NO<sub>x</sub> purifying rate is acquired. This is CeO<sub>2</sub>. A layer is because [ of the 1st catalyst bed (Pd) and the 2nd catalyst bed (Pt, Rh) ] it did and interference with Pd, and Pt and Rh is barred. And when a work example is seen, it turns out that the NO<sub>x</sub> purifying rate is governed by the amount of support of Pt and Rh. Moreover, if the sum total of the amount of support of Pt and Rh shall be 0.8g/L or more, it turns out that a high NO<sub>x</sub> purifying rate is acquired. Moreover, since the improvement in a NO<sub>x</sub> purifying rate is seldom found even if the sum total of the amount of support of Pt and Rh exceeds 1g, it turns out that what is necessary is for this total quantity just to be 1.0g/L or more.

[0034] [HC light-off performance] With the method of preparation of the above-mentioned catalyst, the amount of HC sorbent support of the 1st catalyst bed per 1l. of carriers 130g, The amount of support which doubled Pt and Rh of 7g and the 2nd catalyst bed for the amount of Pd support shall be 1.6g/L, and it is CeO<sub>2</sub>. Some kinds of catalysts which shall be mutually different in the amount of support were prepared. And after giving the heat-treatment same for these catalysts as the case of the point, each catalyst was included in mimesis exhaust gas circulation equipment, and exhaust gas temperature (HC T50) in case it becomes 50%, the light-off temperature, i.e., HC purifying rate, of HC, was investigated. Measurement conditions are the same as the case of evaluation of the above-mentioned NO<sub>x</sub> depuration performance except for the air-fuel ratio of mimesis exhaust gas. It was made to change by the width of 0.9 [ \*\*] focusing on A/F=14.7 about the air-fuel ratio of mimesis exhaust gas. The frequency of this change was 1Hz.

[0035] A result is combined with the thing of the above-mentioned comparative example 1, and is shown in drawing 3 . According to this figure, a work example is understood that light-off temperature is low and HC purifying performance is higher than a comparative example 1. And it is CeO<sub>2</sub> when a work example is seen. The light-off temperature of HC in case the amount of support is 15g/L is the lowest, and also when this amount of support becomes less than this and it increases, light-off temperature is high. CeO<sub>2</sub> [ that HC light-off temperature is high when there are few amounts of support ] Pd of the 1st catalyst bed, and Pt and Rh of the 2nd catalyst bed interfere mutually, and it thinks because those catalyst functions are no longer exhibited fully. CeO<sub>2</sub> As for HC light-off temperature being high when the amount of support increases, the spreading diffusion of HC to the 1st catalyst bed is CeO<sub>2</sub>. It thinks because it is barred. Moreover, this figure to CeO<sub>2</sub> If the amount of support shall be 15-100g/L, it turns out that high HC purifying rate is acquired.

[0036] [The amount of Pd support, HC light-off performance], etc. Proton type Y zeolite (cay van ratio 80) powder is supported by the honeycomb-like MONORISU carrier made from cordierite so that the amount of support may become 130g/L by the wash coat method. Two or more sorts of catalysts which this coat layer comes to support with the various amounts of support by the sinking-in method in Pd were prepared. And change of HC light-off temperature over change of the amount of Pd support was investigated using these catalysts. The describing [ above ] wash coat method and the sinking-in method are the same as the procedure when preparing a previous catalyst, and the measurement conditions and procedure of HC light-off performance of them are also the same as that of the point.

[0037] The result is shown in drawing 4 . According to this figure, if the amount of Pd support is increased, HC light-off temperature will fall, but if it becomes more than a certain quantity, the fall of HC light-off temperature will not progress so much. The relation between such an amount of Pd support and HC light-off performance is also the same as when a rare-earths oxide layer and the 2nd catalyst bed are prepared, therefore the said thing with appropriate the amount of Pd support being 6g/L or more is made for improvement in HC light-off performance.

[0038] The slurry was produced by setting 500g of super-stabilization Y type zeolite (cay van ratio 30) powder, 150g of hydrated alumina powder (binder), and Water 1.5L as a preparation-HC sorbent of the catalyst of the <work-example 2>-work example 2, and carrying out churning mixture. This carrier was made to support HC sorbent of the specified quantity by performing a wash coat to the same carrier as a work example 1 using this slurry.

[0039] Next, the 1st catalyst bed was formed in the surface of each HC adsorbent particle by preparing Pd concentration 4.4wt% of palladium nitrate solution [ 200g of ], and performing calcination (500 degree-Cx 2 hours), after infiltrating altogether HC sorbent coat layer of the above-mentioned carrier and drying this.

[0040] Next, it is CeO<sub>2</sub> on the 1st catalyst bed of each HC adsorbent particle by preparing Ce concentration 6.0wt% of cerium nitrate solution [ 640g of ] by dissolving a cerium nitrate in purified water, and performing same calcination, after infiltrating this into the above-mentioned HC adsorbent layer altogether and drying it. The layer was formed.

[0041] Next, by mixing nitric acid platinum-P salt solution and nitric acid rhodium solution It is CeO<sub>2</sub> of each HC adsorbent particle by preparing Rh concentration 0.17wt% of mixed solution [ 200g of ], and performing same calcination Pt concentration 0.87wt%, after infiltrating this into the above-mentioned HC adsorbent layer altogether and drying it. The 2nd catalyst bed which uses Pt and Rh as catalyst metal was formed on the layer.

[0042] 150g/L and the amount of Pd support of the above-mentioned carrier are [ the acquired catalyst / the amount of support of 1.3L and HC sorbent ] 7g/L and CeO<sub>2</sub>. The amount of support with which the amount of support doubled 36g/L, and Pt and Rh was 1.6g/L (however,



Pt:Rh=5:1).

[0043] - HC sorbent coat layer was formed in the carrier, and this was made to support Pd by the sinking-in method like the preparation-work example 2 of the catalyst of a comparative example 2. And Pt concentration 3.7wt% which mixes nitric acid platinum-P salt solution and nitric acid rhodium solution, It is CeO<sub>2</sub> to Rh concentration 0.74wt% of mixed solution [ 100g of ]. It calcinated by evaporating moisture by performing mixed churning, having thrown in 100g of powder and heating on a hot plate (500 degree-Cx 2 hours). CeO<sub>2</sub> with which this Pt and Rh were supported The slurry was obtained by carrying out churning mixture of 100g of powder, and 15g of hydrated alumina and purified water 300mL. The wash coat was performed on HC sorbent coat layer of the above-mentioned carrier using this slurry.

[0044] Therefore, the catalyst of the acquired comparative example 2 is CeO<sub>2</sub> with which HC adsorbent layer with which the layer of two upper and lower sides is formed on the carrier, and the substratum supported Pd, and the upper layer supported Pt and Rh. It is a layer. Moreover, as for a carrier, as for 1.3L and the amount of HC sorbent support, 150g/L and the amount of Pd support are CeO<sub>2</sub> which supported 7g/L, and Pt and Rh. The amount of support is 38g/L (however, Pt:Rh=5:1).

[0045] - Like the preparation-work example 2 of the catalyst of a comparative example 3, form HC sorbent coat layer in a carrier, use cerium nitrate solution for this coat layer, and it is CeO<sub>2</sub> by the same sinking-in method. An equivalent amount was made to support and an equivalent amount of Pd(s) were made to support by the same sinking-in method further using palladium nitrate solution. Therefore, the point that the catalyst of the acquired comparative example 3 does not have Pt and Rh will be different from the catalyst of a work example 2.

[0046] - Form HC sorbent coat layer in a carrier like the preparation-work example 2 of the catalyst of a comparative example 4. Cerium nitrate solution is used for this coat layer, and it is CeO<sub>2</sub> by the same sinking-in method. An equivalent amount was made to support and an equivalent amount of Pt(s) and Rh(s) were made to support by the same sinking-in method further using the mixed solution of nitric acid platinum-P salt solution and nitric acid rhodium solution. Therefore, the point that the catalyst of the acquired comparative example 4 does not have Pd will be different from the catalyst of a work example 2.

[0047] - About evaluation-above-mentioned each catalyst of the catalyst, it included in the exhaust air system of the car which carries a 3000 cc V type 6-cylinder engine, respectively, and exhaust gas cleaning capacity was evaluated by running mode LA-4. A result is as being shown in Table 1.

[0048]

[Table 1]

	Y1モード		LA-4トータル	
	HC浄化率	NO <sub>x</sub> 浄化率	HC浄化率	NO <sub>x</sub> 浄化率
実施例2	88.5%	82.1%	94.2%	80.1%
比較例2	87.2%	84.0%	93.6%	81.8%
比較例3	89.6%	79.5%	94.4%	71.4%
比較例4	84.2%	85.6%	92.8%	83.4%

[0049] According to this table, in both the work examples 2, HC purifying rate and a NO<sub>x</sub> purifying rate are high. [ the thing with the work example 2 higher / HC purifying rate / and the comparative example 2 higher / a NO<sub>x</sub> purifying rate / when a work example 2 is compared with a comparative example 2 ] At a work example 2, it is CeO<sub>2</sub> on the 1st catalyst bed (Pd) of each HC adsorbent particle. CeO<sub>2</sub> [ thickness / to the layer being formed / in a comparative example 2 ] It is because it is formed so that a layer may cover the whole HC adsorbent layer. According to the comparative example 3, since there are not Pt and Rh, the NO<sub>x</sub> purifying rate is low, and by the comparative example 4, since there is no Pd, HC purifying rate is low.

[0050] The catalyst of a <work-example 3>-work example and the preparation-work example 2 of each catalyst of a comparative example, and the work example 3 of the structure same to the same procedure as \*\*\*\*\* was prepared. A catalyst uses the H type super-stabilization Y type zeolite of 80 as an HC sorbent, and the catalyst of this work example 3 is CeO<sub>2</sub>. The point that the amount of support is 35g/L is different from the catalyst of a work example 2. Moreover, each catalyst of the following comparative examples 5-9 was prepared.

[0051] Comparative examples 5 are the kind of HC sorbent, and CeO<sub>2</sub>, although it is the catalyst of the same structure as the previous comparative example 2. Other conditions, such as the amount of support, were made the same as a work example 3.

[0052] The catalyst of a comparative example 6 is CeO<sub>2</sub> which supported HC adsorbent layer and Pd on the carrier. A layer and CeO<sub>2</sub> which supported Pt and Rh A layer is formed sequentially from the bottom and it is the kind of HC sorbent, and CeO<sub>2</sub>. Other conditions, such as the amount of support, were made the same as a work example 3.

[0053] The catalyst of a comparative example 7 forms HC adsorbent layer on a carrier, and this HC adsorbent layer is made to support Pt and Rh by the sinking-in method. CeO<sub>2</sub> which supported Pd on it A layer is formed and it is this CeO<sub>2</sub>. A layer is made to support Pt and Rh by the sinking-in method, and it is the kind of HC sorbent, and CeO<sub>2</sub>. Other conditions, such as the amount of support, were made the same as a work example 3.

[0054] Form HC adsorbent layer on a carrier, this is made to carry out sinking-in support of these in the order of CeO<sub>2</sub> ->Pd->Pt and Rh, and the catalysts of a comparative example 8 are the kind of HC sorbent, and CeO<sub>2</sub>. Other conditions, such as the amount of support, were made the same as a work example 3.

[0055] The catalyst of a comparative example 9 is CeO<sub>2</sub> which formed HC adsorbent layer on the carrier and supported Pd, Pt, and Rh. A layer is formed with a wash coat on the above-mentioned HC adsorbent layer, and it is the kind of HC sorbent, and CeO<sub>2</sub>. Other conditions, such as the amount of support, were made the same as a work example 3.

[0056] - After heat-treating for evaluation-above-mentioned each catalyst of a catalyst, each catalyst was included in mimesis exhaust gas circulation equipment, and a NO<sub>x</sub> purifying rate (NO<sub>x</sub> C400) in case the inlet gas temperature of each catalyst is 400 degrees C, and the light-off temperature (HC T50) of HC were investigated. The conditions of heat-treatment in this case, the conditions of measurement, and a procedure are the same as it of a work example 1, and the result is shown in Table 2.

[0057]

[Table 2]

	実施例	比較例				
	3	5	6	7	8	9
NO <sub>x</sub> C400(%)	18	19	21	17	7	5
HC T50 (°C)	268	277	296	298	292	265

[0058] According to this table, both the work examples 3 have the depuration performance of HC, and the high depuration performance of NO<sub>x</sub>. Comparative examples 5 and 6 are thickness CeO<sub>2</sub> here. Since the layer has covered the whole HC adsorbent layer, it is HC. T50 becomes high. Since it is separated from comparative examples 7 and 8 of Pd and HC sorbent, it is HC. Since T50 becomes high and, as for comparative examples 8 and 9, Pd, Pt, and Rh are approaching, it is NO<sub>x</sub>. C400 is accepted to be low.

#### [Brief Description of the Drawings]

[Drawing 1] The sectional view showing the catalyst structure of a work example 1

[Drawing 2] The graphical representation showing the relation between a NO<sub>x</sub> purifying rate in case catalyst inlet gas temperature is 400 degrees C, and the amount of Pt-Rh support

[Drawing 3] CeO<sub>2</sub> Graphical representation showing the relation between the amount of support, and the light-off temperature in HC depuration

[Drawing 4] The graphical representation showing the relation between the amount of Pd sinking-in support, and the light-off temperature in HC depuration

[Explanations of letters or numerals]

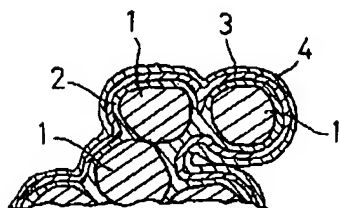
1 HC Adsorbent Particle

2 1st Catalyst Bed

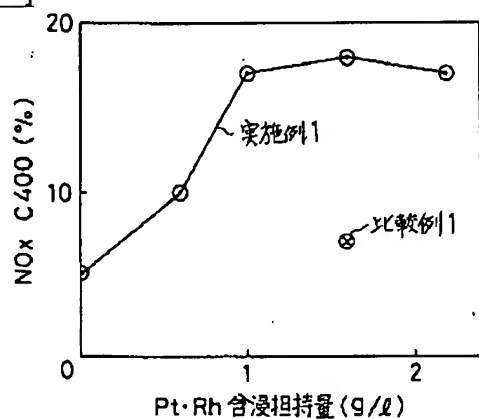
3 CeO<sub>2</sub> Layer (Rare-Earths Oxide Layer)

4 2nd Catalyst Bed

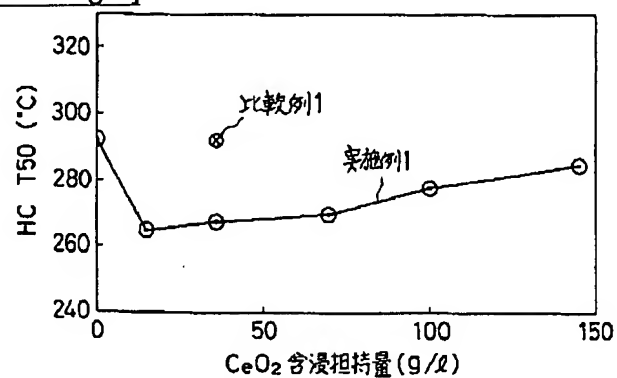
[Drawing 1]



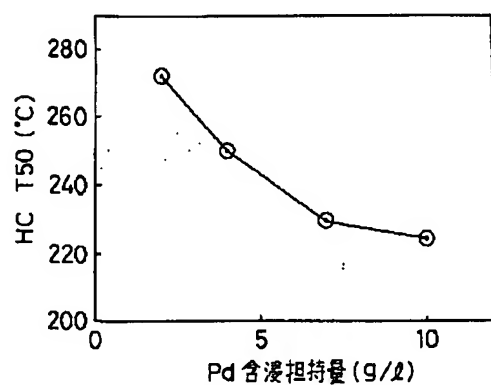
[Drawing 2]



[Drawing 3]



[Drawing 4]



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L2: Entry 2 of 2

File: DWPI

Jun 25, 1996

DERWENT-ACC-NO: 1996-349304

DERWENT-WEEK: 199642

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TITLE: Purificn. catalyst for exhaust gas from IC engine - where monolithic catalyst has coating of e.g. crystalline aluminosilicate prim. catalyst layer contg. palladium and rare earth metal oxide, and sec. catalyst layer

## PATENT-ASSIGNEE:

ASSIGNEE

CODE

MATSUDA KK

MAZD

PRIORITY-DATA: 1994JP-0307831 (December 12, 1994)

[Search Selected](#)[Search ALL](#)[Clear](#)

## PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
<input type="checkbox"/> <a href="#">JP 08164338 A</a>	June 25, 1996		007	B01J029/068

## APPLICATION-DATA:

PUB-NO	APPL-DATE	APPL-NO	DESCRIPTOR
JP 08164338A	December 12, 1994	1994JP-0307831	

INT-CL (IPC): B01D 53/34; B01D 53/72; B01D 53/86; B01D 53/94; B01J 29/068; B01J 29/12

ABSTRACTED-PUB-NO: JP 08164338A

## BASIC-ABSTRACT:

The catalyst is composed of monolith support material coated by HC adsorbent eg. crystalline aluminosilicate, coated by prim. catalyst layer contg. Pd, covered by rare earth metal oxide such as ceria at 15-100 g/lL support and laminated by sec. catalyst layer contg. Pt or Rh.

ADVANTAGE - HC and NO are removed at high efficiency.

CHOSEN-DRAWING: Dwg.4/4

TITLE-TERMS: PURIFICATION CATALYST EXHAUST GAS IC ENGINE MONOLITHIC CATALYST COATING CRYSTAL ALUMINOSILICATE PRIMARY CATALYST LAYER CONTAIN PALLADIUM RARE EARTH METAL OXIDE SEC CATALYST LAYER

DERWENT-CLASS: H06 J01 J04

CPI-CODES: H06-C03A; H06-C03B; J01-E02D; J04-E04; N01-C01A; N02-F02; N03-A;

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

A545 A546 A678 A700 A758 C810 M411 M730 M903 Q421

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1784U

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1996-110189

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L2: Entry 1 of 2

File: JPAB

Jun 25, 1996

PUB-NO: JP408164338A

DOCUMENT-IDENTIFIER: JP 08164338 A

TITLE: EXHAUST GAS PURIFYING CATALYST FOR INTERNAL COMBUSTION ENGINE

PUBN-DATE: June 25, 1996

## INVENTOR-INFORMATION:

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ICHIKAWA, TOMOJI

KUROKAWA, TAKAHIRO

## ASSIGNEE-INFORMATION:

NAME

COUNTRY

MAZDA MOTOR CORP

APPL-NO: JP06307831

APPL-DATE: December 12, 1994

INT-CL (IPC): B01J 29/068; B01D 53/34; B01D 53/72; B01D 53/86; B01D 53/94; B01J 29/12

## ABSTRACT:

PURPOSE: To provide a catalyst for preventing discharge of unpurified HC at a cold time of an internal combustion engine and enabling to efficiently decompose HC and NOx in the exhaust gas at the later time.

CONSTITUTION: A first layer 2 in which Pd is a catalyst metal, a rare earth oxides layer 3 and a second catalyst layer 4 in which Pt, Rh are catalyst metals are successively formed on surfaces of each HC adsorbent particle 1 consisting of inorganic crystalline molecular sheaves on a carrier 1.

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B 0 1 J 29/068	Z A B A			
B 0 1 D 53/34	Z A B			
53/72				

B 0 1 D 53/ 34 Z A B  
1 2 0 D

審査請求 未請求 請求項の数 4 O L (全 7 頁) 最終頁に続く

(21) 出願番号 特願平6-307831

(22) 出願日 平成6年(1994)12月12日

(71) 出願人 000003137

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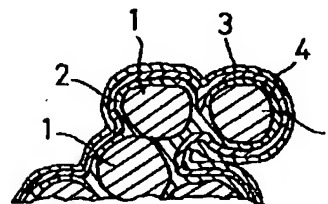
(74) 代理人 弁理士 前田 弘 (外2名)

(54) 【発明の名称】 内燃機関の排気ガス浄化用触媒

(57) 【要約】

【目的】 内燃機関の冷間時における未浄化HCの排出を防止するとともに、その後の排気ガス中のHC及びNO<sub>x</sub>を効率良く分解することができる触媒を提供する。

【構成】 担体1の上の無機結晶性モレキュラーシーブよりなる各HC吸着剤粒子1の表面に、Pdを触媒金属とする第1触媒層2、希土類酸化物層3及びPt、Rhを触媒金属とする第2触媒層4が順に形成されている。



## 【特許請求の範囲】

【請求項1】 担体の上に、排気ガス中の炭化水素を吸着する粉末状の無機結晶性モレキュラーシーブよりなるHC吸着剤が担持されていて、

上記HC吸着剤粒子の各々の表面にPdを触媒金属とする第1触媒層が形成され、

上記第1触媒層の上に、希土類酸化物を主成分とする希土類酸化物層が形成され、

上記希土類酸化物層の上に、Pt及びRhのうちの少なくとも一方を触媒金属とする第2触媒層が形成されていることを特徴とする内燃機関の排気ガス浄化用触媒。

【請求項2】 請求項1に記載されている内燃機関の排気ガス浄化用触媒において、

上記希土類酸化物がCeO<sub>2</sub>であることを特徴とする内燃機関の排気ガス浄化用触媒。

【請求項3】 請求項3に記載されている内燃機関の排気ガス浄化用触媒において、

上記担体がモノリス担体であって、該担体1リットル当たりの上記CeO<sub>2</sub>の量が15～100gであることを特徴とする内燃機関の排気ガス浄化用触媒。

【請求項4】 請求項1に記載されている内燃機関の排気ガス浄化用触媒において、

上記HC吸着剤が結晶性アルミノシリケートであることを特徴とする内燃機関の排気ガス浄化用触媒。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は内燃機関の排気ガス浄化用触媒に関する。

## 【0002】

【従来の技術】 内燃機関の排気ガス中のHC（炭化水素）、CO（一酸化炭素）及びNO<sub>x</sub>（窒素酸化物）を浄化する触媒として、モノリス担体の上にゼオライトを主成分とする第1触媒層を設け、該第1触媒層の上に酸化還元能を備えた貴金属触媒を主成分とする第2触媒層を設けてなるものが知られている（特開平2-56247号公報参照）。上記第1触媒層には必要に応じてPt、Pd、Rh等の貴金属やCeO<sub>2</sub>（セリア）、La<sub>2</sub>O<sub>3</sub>（ランタナ）等の希土類酸化物が担持され、上記第2触媒層はアルミナコート層にPt、Pd、Rh等の貴金属が担持され、必要に応じて上記希土類酸化物や酸化ジルコニウム等が担持される。

【0003】 上記排気ガス浄化用触媒は、内燃機関の冷間時で且つ空燃比がリッチの状態にあるときに排気ガス中のHCを上記第1触媒層のゼオライトによって吸着し、暖機によって排気ガス温度及び触媒温度が上昇したときに、上記第1触媒層から脱離するHC、排気ガス中のHC及びCOの酸化とNO<sub>x</sub>の還元とを上記第2触媒層によって行なうものである。

## 【0004】

【発明が解決しようとする課題】 本発明者は、上記P

t、Pd及びRhの触媒金属としての機能に関し、Pt及びPdは酸化能が高いが、それに比べてRhは酸化能が低いこと、従って、Pt及びPdはHCの浄化に有効であること、また、PtとRhとを組み合わせた場合にはHCの酸化と共にNO<sub>x</sub>の分解が比較的効率良く進む、という知見を得ていた。

【0005】 しかし、上記従来技術において、上記第1触媒層の触媒金属又は第2触媒層の触媒金属として上記Pt、Pd及びRhの三者を併用した場合には、PtとRhとを併用した場合に比べてHC浄化率及びNO<sub>x</sub>浄化率が共に低下するという問題がある。これはPt、RhとPdとが互いの触媒機能を阻害するように干渉し合うためと考えられる。これに対して、例えばPdを第1触媒層に、PtやRhを第2触媒層にそれぞれ担持させることにより、PdをPtやRhから離すことが考えられるが、第1触媒層と第2触媒層との界面においてPdとPt、Rhとが接触し、必ずしも好結果が得られない。

【0006】 そこで、本発明は、上記Pdをその本来の触媒機能が発揮されるように上記PtやRhと組み合わせ、内燃機関の冷間時及び暖機後のHC浄化率を高めるとともに、NO<sub>x</sub>浄化率を高めようとするものである。

## 【0007】

【課題を解決するための手段及びその作用】 本発明者は、上記課題に対して種々の実験及び検討を加えた結果、Pdを触媒金属とする第1触媒層と、Pt又はRhを触媒金属とする第2触媒層との間に希土類酸化物の層を介在させたときに、これらの触媒金属及びHC吸着剤の各々がその本来の有する機能を有効に発揮し、所期の目的を達成することができること、特に上記第1触媒層、希土類酸化物層及び第2触媒層をHC吸着剤粒子の各々の表面に形成した場合に好結果が得られることを見出し、本発明を完成するに至ったものである。以下、各請求項に係る発明を具体的に説明する。

【0008】 <請求項1に係る発明> この発明は、担体の上に、排気ガス中の炭化水素を吸着する粉末状の無機結晶性モレキュラーシーブよりなるHC吸着剤が担持されていて、上記HC吸着剤粒子の各々の表面にPdを触媒金属とする第1触媒層が形成され、上記第1触媒層の上に、希土類酸化物を主成分とする希土類酸化物層が形成され、上記希土類酸化物層の上に、Pt及びRhのうちの少なくとも一方を触媒金属とする第2触媒層が形成されていることを特徴とする内燃機関の排気ガス浄化用触媒である。

【0009】 当該発明においては、内燃機関の冷間時には排気ガス中のHCがHC吸着剤に吸着されて、未浄化HCの排出が防止される。暖機によって排気ガス温度及び触媒温度が上昇してくると、各HC吸着剤に吸着されていたHCの脱離が始まるが、この各HC吸着剤粒子の表面にはPdを触媒金属とする第1触媒層が形成されて

いるから、当該脱離HCはPdに接触し易く、このため、Pdが当該HCを酸化分解する触媒機能を効率良く発揮する。また、第2触媒層においても、上記脱離するHCがPt又はRhによって分解されるが、このPtやRhは排気ガス中のNOxの浄化に有効な触媒金属であり、上記脱離・分解するHCを還元剤としてNOxを還元分解する触媒機能を発揮する。また、内燃機関から新たに排出されるHCやCOも第1触媒層及び第2触媒層の触媒金属によって酸化分解され、このような酸化反応に伴ってNOxの還元分解反応が進行する。

【0010】一方、上記第1触媒層と第2触媒層との間に介在する希土類酸化物は、上記PtやRhとPdとが干渉し合うことを妨げるバリアの機能を果たし、これらの触媒金属間の相互作用による触媒機能の低下が防止される。一方、このようなバリアが排気ガス中のHCの拡散をも妨げるものであるならば、第1触媒層がHCの吸着・分解に有効に利用されないことになるが、当該発明のバリアは希土類酸化物であり、この希土類酸化物はHCの拡散を若干妨げるとしてもその程度は低く、第1触媒層のHC吸着剤による排気ガス中のHCの吸着の支障

にはならない。かえって、この希土類酸化物はO<sub>2</sub> ストレージ効果を有するから、第1触媒層及び第2触媒層におけるHCの酸化に有効に寄与することになる。

【0011】しかして、当該発明の場合は、HC吸着剤粒子の各々の表面上に上記第1触媒層、希土類酸化物層及び第2触媒層が形成されているから、個々のHC吸着剤粒子の上でHCの酸化分解とNOxの還元分解を生じ各々の浄化率が高くなる。

【0012】ここに、上記担体としては、モノリス担体であっても、ペレット状の担体であってもよい。また、上記HC吸着剤としての無機結晶性モレキュラーシーブとしては、結晶の骨格(結晶格子)を形成する金属としてAlを用いたアルミノシリケート(Yゼオライト、モルデナイト、ZSM5、ベータゼオライトなど各種のゼオライト)、Alに代えて或いはAlと共にGa、Ce、Mn、Tbなど他の金属を用いた他の結晶質多孔の金属含有シリケート、さらには、ほとんどシリカだけからなるものや、Siを含まないものなど種々のものを採用することができる。

【0013】<請求項2に係る発明>この発明は、上記

請求項1に記載されている内燃機関の排気ガス浄化用触媒において、上記希土類酸化物がCeO<sub>2</sub>であることを特徴とする内燃機関の排気ガス浄化用触媒である。

【0014】この発明において、希土類酸化物としてCeO<sub>2</sub>を用いるのは、該CeO<sub>2</sub>のO<sub>2</sub> ストレージ効果が高く、HCの酸化分解に有利になるためである。

【0015】<請求項3に係る発明>この発明は、上記請求項3に記載されている内燃機関の排気ガス浄化用触媒において、上記担体がモノリス担体であって、該担体1リットル当たりの上記CeO<sub>2</sub>の量が15~100g

であることを特徴とする内燃機関の排気ガス浄化用触媒である。

【0016】当該発明において、モノリス担体を用いるのは排気ガスと触媒層との接触に有利になるからであり、また、触媒の小型・軽量化が図れ、背圧の上昇も少ないからである。また、担体1リットル当たりのCeO<sub>2</sub>量を15以上とするのは第1触媒層のPdと第2触媒層のPt又はRhとを遮断する効果を確保するためであり、CeO<sub>2</sub>量を100g以下とするのは、これよりもその量が多くなると第2触媒層から第1触媒層へのHCの拡散に不利になるためである。

【0017】<請求項4に係る発明>この発明は、上記請求項1に記載されている内燃機関の排気ガス浄化用触媒において、上記HC吸着剤が結晶性アルミノシリケートであることを特徴とする内燃機関の排気ガス浄化用触媒である。

【0018】当該発明において、HC吸着剤として上記アルミノシリケートを用いるのは、これが耐熱性を有し且つそのHC吸着能が高いためである。

【0019】

【発明の効果】請求項1に係る発明によれば、各HC吸着剤粒子の上にPdを触媒金属とする第1触媒層と、Pt又はRhを触媒金属とする第2触媒層と、希土類酸化物層とを形成し、且つ第1触媒層と第2触媒層との間に希土類酸化物層を介在させたから、第2触媒層から第1触媒層へのHCの拡散を許容しながら、Pt又はRhとPdとが干渉し合うことを避けてPdの触媒機能を充分に発揮させることができ、冷間時における未浄化HCの排出を防止しながら、該HC及びNOxを効率良く浄化することができ、しかも各HC吸着剤粒子の上でHC及びNOxの分解浄化が行なわれるから、高いHC浄化率及び高いNOx浄化率が得られる。

【0020】請求項2に係る発明によれば、上記希土類酸化物としてCeO<sub>2</sub>を用いたから該CeO<sub>2</sub>の高いO<sub>2</sub> ストレージ効果をHCの酸化分解に利用することができ、HC浄化率及びNOx浄化率の向上に有利になる。

【0021】請求項3に係る発明によれば、上記CeO<sub>2</sub>の量をモノリス担体1リットル当たり15~100gとしたから、第2触媒層から第1触媒層へHCを拡散させながら、第1触媒層のPdと第2触媒層のPt又はRhとの接触を避ける上で有利になる。

【0022】請求項4に係る発明によれば、上記HC吸着剤として結晶性アルミノシリケートを用いたから、触媒のHC吸着能が高まり、HC浄化率及びNOx浄化率の向上に有利になる。

【0023】

【実施例】以下、本発明の実施例を図面に基づいて説明する。

【0024】<実施例1>

—触媒の調製—

H<sub>2</sub>C吸着剤としてプロトン型のYゼオライト(ケイバン比80)粉末をコーゼライト製ハニカム状のモノリス担体(400セル/inch<sup>2</sup>)にウォッシュコートした。このウォッシュコートは、上記Yゼオライトとバインダとしての水和アルミナとを100:20の重量比で合わせ適量の純水を加えて攪拌混合することによりスラリーを作製し、該スラリーに上記担体を浸漬し引き上げて余分なスラリーを吹き飛ばし乾燥するという工程を繰り返すことによって所定量のYゼオライトを上記担体に担持させた後に、500℃×2時間の焼成を行なう、というものである。

【0025】次に、上記ウォッシュコート層にPdを含浸法によって担持させることによって第1触媒層を形成した。この含浸担持は、所定濃度の硝酸パラジウム水溶液を上記ウォッシュコート層に含浸させ乾燥及び焼成(500℃×2時間)を行なう、というものである。

【0026】次に、硝酸セリウムを純水に溶解して硝酸セリウム水溶液を調製し、該硝酸セリウム水溶液を上記ウォッシュコート層に含浸させ、乾燥・焼成を行なうことによって上記第1触媒層の上に希土類酸化物層としてのCeO<sub>2</sub>層を形成した。

【0027】次に硝酸白金-Pソルト溶液(ジニトロジアミン白金(II)硝酸酸性水溶液)と硝酸ロジウム水溶液とを混合し、該混合水溶液を上記ウォッシュコート層に含浸させることによって、Pt及びRhを触媒金属とする第2触媒層を上記CeO<sub>2</sub>層の上に形成した。

【0028】従って、本例の触媒構造は図1に示すように、担体上の各H<sub>2</sub>C吸着剤粒子1の表面に第1触媒層2、CeO<sub>2</sub>層3及び第2触媒層4が下から順に積層形成されたものになっている。

【0029】-触媒の評価-

[NO<sub>x</sub>浄化性能] 上記触媒の調製法によって、担体1リットル当たりの第1触媒層のH<sub>2</sub>C吸着剤担持量を130g、Pd担持量を7g、CeO<sub>2</sub>担持量を36gとし、第2触媒層のPt及びRhを合わせた担持量を互いに異なるものとした数種類の触媒を調製した。PtとRhとの重量比率はいずれも5:1とした。そして、これらの触媒に加熱処理を施した後に各触媒を模擬排気ガス流通装置に組み込み、各触媒の入口ガス温度が40.0℃の時のNO<sub>x</sub>浄化率(NO<sub>x</sub>-C400)を調べた。測定条件は次の通りである。

【0030】加熱処理; 900℃×50時間(大気中) 模擬排気ガス; 成分 N<sub>2</sub>, CO<sub>2</sub>, CO, C<sub>3</sub>H<sub>6</sub>, O<sub>2</sub>, H<sub>2</sub>, NO但し、A/F=15.0であり、H<sub>2</sub>Oを10%添加している。

空間速度; SV=6000h<sup>-1</sup>

模擬排気ガスの昇温速度; 30度/分(室温から500℃まで昇温)

【0031】模擬排気ガスのA/F値を理論空燃比よりもリーン側に設定したのは、触媒によるNO<sub>x</sub>の浄化を

難しいものとして、各触媒に性能差が出やすいようにするためである。

【0032】結果は図2に比較例1のものと併せて示されている。比較例1は実施例と同じ担体にH<sub>2</sub>C吸着剤のウォッシュコートを行なった後に、CeO<sub>2</sub>→Pd→Pt, Rhの順で含浸担持を行なったものであり、含浸の順序は異なるが、ウォッシュコート法及び含浸法、並びに材料は実施例と同じである。また、比較例1のH<sub>2</sub>C吸着剤担持量は130g/L、Pd担持量は7g/L、CeO<sub>2</sub>担持量を36g/L、Pt及びRhを合わせた担持量は1.6g/Lである。

【0033】同図によれば、実施例では高いNO<sub>x</sub>浄化率が得られることがわかる。これはCeO<sub>2</sub>層が第1触媒層(Pd)と第2触媒層(Pt, Rh)との間にあって、PdとPt及びRhとの干渉を妨げているためである。そして、実施例をみるとNO<sub>x</sub>浄化率はPt及びRhの担持量に支配されていることがわかる。また、Pt及びRhの担持量の合計を0.8g/L以上にすれば、高いNO<sub>x</sub>浄化率が得られることがわかる。また、Pt及びRhの担持量の合計が1gを越えてもNO<sub>x</sub>浄化率の向上はあまり見られないことから、該合計量を1.0g/L以上にすればよいことがわかる。

【0034】[H<sub>2</sub>Cライトオフ性能] 上記触媒の調製法によって、担体1リットル当たりの第1触媒層のH<sub>2</sub>C吸着剤担持量を130g、Pd担持量を7g、第2触媒層のPt及びRhを合わせた担持量を1.6g/Lとし、CeO<sub>2</sub>担持量を互いに異なるものとした数種類の触媒を調製した。そして、これらの触媒に先の場合と同じ加熱処理を施した後に各触媒を模擬排気ガス流通装置に組み込み、H<sub>2</sub>Cのライトオフ温度、すなわち、H<sub>2</sub>C浄化率が50%になるときの排気ガス温度(HC-T50)を調べた。測定条件は模擬排気ガスの空燃比を除いて上記NO<sub>x</sub>浄化性能の評価の場合と同じである。模擬排気ガスの空燃比に関しては、A/F=14.7を中心として±0.9の幅で変動させた。この変動の周波数は1Hzとした。

【0035】結果は図3に上記比較例1のものと併せて示されている。同図によれば、実施例は比較例1よりもライトオフ温度が低く、H<sub>2</sub>C浄化性能が高いことがわかる。そして、実施例をみるとCeO<sub>2</sub>担持量が15g/LのときのH<sub>2</sub>Cのライトオフ温度が最も低く、これよりも該担持量が少なくなる場合も多くなる場合もライトオフ温度が高くなっている。CeO<sub>2</sub>担持量が少ない場合にH<sub>2</sub>Cライトオフ温度が高くなっているのは、第1触媒層のPdと第2触媒層のPt及びRhとが互いに干渉し、それらの触媒機能が充分に発揮されなくなるためと考えられ、CeO<sub>2</sub>担持量が多くなった場合にH<sub>2</sub>Cライトオフ温度が高くなっているのは、第1触媒層へのH<sub>2</sub>Cの拡散移動がCeO<sub>2</sub>によって妨げられるためと考えられる。また、同図から、CeO<sub>2</sub>担持量を15~100

g/Lにすれば高いHC浄化率が得られることがわかる。

【0036】[Pd担持量とHCライトオフ性能等について]コーゼライト製のハニカム状モノリス担体にプロトン型のYゼオライト(ケイバン比80)粉末がウォッシュコート法によって担持量が130g/Lとなるように担持され、このコート層にPdを含浸法によって種々の担持量で担持されてなる複数種の触媒を調製した。そして、これらの触媒を用いてPd担持量の変化に対するHCライトオフ温度の変化を調べた。上記ウォッシュコート法及び含浸法は先の触媒を調製するときの方法と同じであり、また、HCライトオフ性能の測定条件及び方法も先と同じである。

【0037】結果は図4に示されている。同図によれば、Pd担持量を多くすればHCライトオフ温度が低下するが、ある量以上になるとHCライトオフ温度の低下はそれほど進まなくなっている。このようなPd担持量とHCライトオフ性能との関係は希土類酸化物層及び第2触媒層を設けた場合も同じであり、従って、HCライトオフ性能の向上のためにはPd担持量を6g/L以上

【0038】<実施例2>

—実施例2の触媒の調製—

HC吸着剤として超安定化Y型ゼオライト(ケイバン比30)粉末500g、水和アルミナ粉末(バインダ)150g及び水1.5Lを合わせて攪拌混合することによってスラリーを作製した。このスラリーを用いて実施例1と同様の担体にウォッシュコートを行なうことによって、該担体に所定量のHC吸着剤を担持させた。

【0039】次に、Pd濃度4.4wt%の硝酸パラジウム水溶液200gを調製し、これを上記担体のHC吸着剤コート層に全て含浸させ、乾燥させた後、焼成(500℃×2時間)を行なうことによって、各HC吸着剤粒子の表面に第1触媒層を形成した。

【0040】次に、硝酸セリウムを純水に溶解することによってCe濃度6.0wt%の硝酸セリウム水溶液640gを調製し、これを上記HC吸着剤層に全て含浸させ、乾燥させた後、同様の焼成を行なうことによって、各HC吸着剤粒子の第1触媒層の上にCeO<sub>2</sub>層を形成した。

【0041】次に、硝酸白金-Pソルト溶液と硝酸ロジウム水溶液とを混合することによって、Pt濃度0.87wt%、Rh濃度0.17wt%の混合水溶液200gを調製し、これを上記HC吸着剤層に全て含浸させ、乾燥させた後、同様の焼成を行なうことによって、各HC吸着剤粒子のCeO<sub>2</sub>層の上にPt及びRhを触媒金属とする第2触媒層を形成した。

【0042】得られた触媒は、上記担体が1.3L、H

C吸着剤の担持量が150g/L、Pd担持量が7g/L、CeO<sub>2</sub>担持量が36g/L、Pt及びRhを合わせた担持量が1.6g/L(但し、Pt:Rh=5:1)であった。

【0043】—比較例2の触媒の調製—

実施例2と同様に、担体にHC吸着剤コート層を形成し、これにPdを含浸法によって担持させた。そして、硝酸白金-Pソルト溶液と硝酸ロジウム水溶液とを混合してなるPt濃度3.7wt%、Rh濃度0.74wt%の混合水溶液100gにCeO<sub>2</sub>粉末100gを投入し、ホットプレート上で加熱しつつ混合攪拌を行なうことによって水分を蒸発させ、焼成(500℃×2時間)した。このPt及びRhが担持されたCeO<sub>2</sub>粉末100gと水和アルミナ15gと純水300mLとを攪拌混合することによってスラリーを得た。このスラリーを用いて上記担体のHC吸着剤コート層の上にウォッシュコートを行なった。

【0044】従って、得られた比較例2の触媒は、担体の上に上下2つの層が形成されていて、下層がPdを担持したHC吸着剤層、上層がPt及びRhを担持したCeO<sub>2</sub>層になっている。また、担体は1.3L、HC吸着剤担持量は150g/L、Pd担持量は7g/L、Pt及びRhを担持したCeO<sub>2</sub>の担持量が38g/L(但し、Pt:Rh=5:1)である。

【0045】—比較例3の触媒の調製—

実施例2と同様に、担体にHC吸着剤コート層を形成し、該コート層に硝酸セリウム水溶液を用いて同様の含浸法によってCeO<sub>2</sub>を同量担持させ、さらに、硝酸パラジウム水溶液を用いて同様の含浸法によってPdを同量担持させた。従って、得られた比較例3の触媒はPt及びRhがない点が実施例2の触媒と相違することになる。

【0046】—比較例4の触媒の調製—

実施例2と同様に、担体にHC吸着剤コート層を形成し、該コート層に硝酸セリウム水溶液を用いて同様の含浸法によってCeO<sub>2</sub>を同量担持させ、さらに、硝酸白金-Pソルト溶液と硝酸ロジウム水溶液との混合水溶液を用いて同様の含浸法によってPt及びRhを同量担持させた。従って、得られた比較例4の触媒はPdがない点が実施例2の触媒と相違することになる。

【0047】—触媒の評価—

上記各触媒について、それぞれV型6気筒の3000ccのエンジンを搭載した自動車の排気系に組み込み、走行モードLA-4にて排気ガス浄化性能を評価した。結果は表1に示す通りである。

【0048】

【表1】

	Y1モード		LA-4トータル	
	HC浄化率	NO <sub>x</sub> 浄化率	HC浄化率	NO <sub>x</sub> 浄化率
実施例2	88.5%	82.1%	94.2%	80.1%
比較例2	87.2%	84.0%	93.6%	81.8%
比較例3	89.6%	79.5%	94.4%	71.4%
比較例4	84.2%	85.6%	92.8%	83.4%

【0049】同表によれば実施例2ではHC浄化率及びNO<sub>x</sub>浄化率が共に高い。実施例2と比較例2とを比べた場合、HC浄化率は実施例2の方が高く、NO<sub>x</sub>浄化率は比較例2の方が高いのは、実施例2では各HC吸着剤粒子の第1触媒層(Pd)上にCeO<sub>2</sub>層が形成されているのに対し、比較例2では層厚なCeO<sub>2</sub>層がHC吸着剤層全体を覆うように形成されているためである。比較例3ではPt及びRhがないためにNO<sub>x</sub>浄化率が低くなっており、比較例4ではPdがないためにHC浄化率が低くなっている。

#### 【0050】＜実施例3＞

—実施例及び比較例の各触媒の調製—

実施例2と同様の方法によつて同様の構造の実施例3の触媒を調製した。この実施例3の触媒は、HC吸着剤としてケイバン比が80のH型超安定化Y型ゼオライトを用い、CeO<sub>2</sub>の担持量が35g/Lである点が実施例2の触媒と相違する。また、以下の比較例5～9の各触媒を調製した。

【0051】比較例5は、先の比較例2と同じ構造の触媒であるが、HC吸着剤の種類、CeO<sub>2</sub>の担持量など他の条件を実施例3と同じにした。

【0052】比較例6の触媒は、担体の上にHC吸着剤層、Pdを担持したCeO<sub>2</sub>層、並びにPt及びRhを担持したCeO<sub>2</sub>層が下から順に形成されたものであり、HC吸着剤の種類、CeO<sub>2</sub>の担持量など他の条件を実施例3と同じにした。

\* 【0053】比較例7の触媒は、担体の上にHC吸着剤層を形成し、該HC吸着剤層にPt及びRhを含浸法によって担持させ、その上にPdを担持したCeO<sub>2</sub>層を形成し、該CeO<sub>2</sub>層にPt及びRhを含浸法によって担持させたものであり、HC吸着剤の種類、CeO<sub>2</sub>の担持量など他の条件を実施例3と同じにした。

【0054】比較例8の触媒は、担体の上にHC吸着剤層を形成し、これにCeO<sub>2</sub>→Pd→Pt及びRhの順でこれらを含浸担持させたものであり、HC吸着剤の種類、CeO<sub>2</sub>の担持量など他の条件を実施例3と同じにした。

20 【0055】比較例9の触媒は、担体の上にHC吸着剤層を形成し、Pd、Pt及びRhを担持したCeO<sub>2</sub>層を上記HC吸着剤層の上にウォッシュコートによって形成したものであり、HC吸着剤の種類、CeO<sub>2</sub>の担持量など他の条件を実施例3と同じにした。

#### 【0056】—触媒の評価—

上記各触媒に加熱処理を施した後に各触媒を模擬排気ガス流通装置に組み込み、各触媒の入口ガス温度が400℃の時のNO<sub>x</sub>浄化率(NO<sub>x</sub> C400)と、HCのライトオフ温度(HC T50)を調べた。この場合の加熱処理の条件並びに測定の条件及び方法は実施例1のそれと同じであり、結果は表2に示されている。

#### 【0057】

【表2】

	実施例	比較例				
	3	5	6	7	8	9
NO <sub>x</sub> C400(%)	18	19	21	17	7	5
HC T50(℃)	268	277	296	298	292	265

【0058】同表によれば、実施例3はHCの浄化性能及びNO<sub>x</sub>の浄化性能が共に高い。ここに、比較例5、6は層厚なCeO<sub>2</sub>層がHC吸着剤層全体を覆っているためにHC T50が高くなり、比較例7、8はPdとHC吸着剤とが離れているためにHC T50が高くなり、比較例8、9はPdとPt、Rhとが接近しているためにNO<sub>x</sub> C400が低くなっているものと認められる。

#### 【図面の簡単な説明】

【図1】実施例1の触媒構造を示す断面図

※【図2】触媒入口ガス温度が400℃のときのNO<sub>x</sub>浄化率とPt・Rh担持量との関係を示すグラフ図

【図3】CeO<sub>2</sub>担持量とHC浄化におけるライトオフ温度との関係を示すグラフ図

【図4】Pd含浸担持量とHC浄化におけるライトオフ温度との関係を示すグラフ図

#### 【符号の説明】

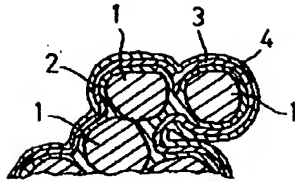
1 HC吸着剤粒子

2 第1触媒層

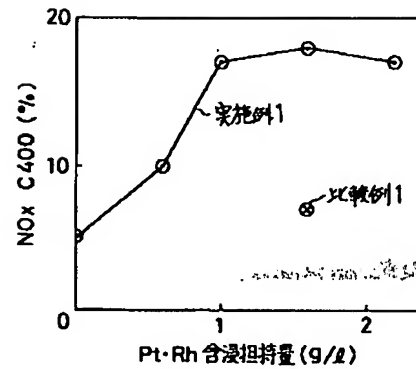
※50 3 CeO<sub>2</sub>層(希土類酸化物層)

## 4 第2触媒層

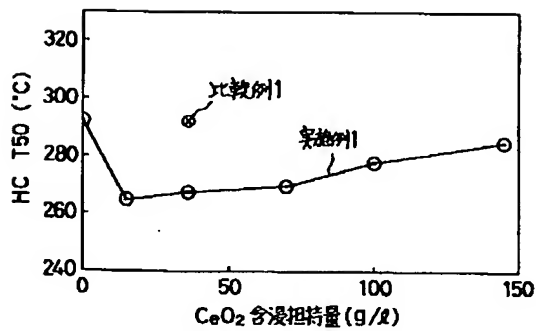
【図1】



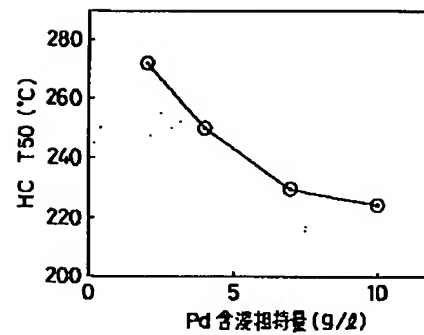
【図2】



【図3】



【図4】



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